Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 805

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July 1999

Submitted to
Journal of Applied Polymer Science

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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PAPER SIZING AGENTS FROM MICELLE-LIKE AGGREGATES OF POLYSTYRENE-BASED CATIONIC COPOLYMERS

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ABSTRACT

A series of polystyrene-based cationic copolymers (PSCC) were synthesized by copolymerization of styrene and cationic comonomer vinylbenzyl trimethylammonium chloride (VBTMAC). These copolymers can be used as internal paper sizing agents in a broad pH range. The effect of charge density on the PSCC colloid properties was investigated. It was found that at room temperature the PSCC could change from water-insoluble to colloidally dispersible and finally to fully water-soluble as the charge density was increased.

Based on the understanding of its colloid behavior, PSCCs were applied as paper internal sizing agents. The results showed that the hydrophobicity of handsheets could be significantly improved by PSCC and the sizing performance was the function of copolymer addition, charge density, particle size, drying temperature, as well as pH conditions.

The present study indicated some potential advantages of PSCC copolymers as internal sizes. PSCC can be self-retained on the fiber surface, no hydrolysis occurs during the storage and application, and no sizing reversion occurs.

INTRODUCTION

Cellulosic materials usually are hydrophilic; therefore, paper fibers have a strong natural tendency to interact with water. Paper products like towels and tissues adsorb water rapidly. However, for many paper grades designed for use in writing, printing, packaging, and construction, liquid repellency is essential. Sizing is the process of making papers more water-resistant by using sizing agents during papermaking. The commonly used sizing agents include rosin-based natural sizes and synthetic sizes such as alkylketene dimer (AKD) and alkenyl succinic anhydride (ASA). The North American market for these sizing agents exceeds 250 million pounds in 1999 [1]. The worldwide demand is estimated around $300 million in sales of rosin sizes and $250 million in sales of synthetic sizes, with annual market growth of between 4% and 5%.

However, the commercially used sizing agents cannot fully satisfy the papermaker's requirements. It is well known that rosin-based sizing agents are restricted only under acidic conditions. Although AKD and ASA can be used for alkaline papermaking, some problems, such as paper slipperiness, low emulsion instability, hydrolysis, deposition on paper machine, and sizing reversion, often occur during papermaking.

To be a potential sizing agent, the material must meet certain criteria. It must be highly hydrophobic, must have high retention on the fibers, distribute uniformly, and be chemically stable with penetrants [2, 3]. Polymeric sizing agent is a new member in the family of sizing materials. Polymer sizes have some advantages over the conventional used ones, such as high hydrophobicity, good stability, and ease of modification. Much research has been undertaken in this area [4-8].

For the present study, a polystyrene-based cationic copolymer (PSCC) was chosen as the internal sizing agent. Pure polystyrene is a hydrophobic material. In order to get a uniform distribution onto fiber surfaces, the polymer has to be prepared into small

particles. In addition, these particles should be able to attach to fibers. Recent studies reported that the cationically charged polystyrene latexes are effective papermaking retention aids and sizing agents [9-12]. The cationic nature enables the adhesion between polymer and fibers. In order to improve the uniformity of the polymer adsorption and diffusion on wood fiber surfaces, the particle size of PSCC should be less than 100 nm [10]. Both emulsion and microemulsion polymerization techniques have been used for cationic latexes preparation in previous works [9-12]. However, it was found that the conventional emulsion polymerization technique is difficult to use for preparing such small particles. Although microemulsion technique has been successfully used, the high surfactant concentration used in microemulsion polymerization will reduce the hydrophobicity of wood fibers, which gives a negative effect on the paper sizing. Furthermore, the high dosage of surfactant will increase the cost. In this work, a new approach for preparing very small particles of PSCC was reported.

To consider a material a good sizing agent, it should meet the criteria mentioned earlier. A polystyrene-based cationic copolymer (PSCC) could meet these features well. First, cationic repeat units along the polymer molecule would serve as a retention aid. Second, polystyrene would provide high hydrophobicity. Finally, the uniform distribution could be achieved through the small particles, which sizes can be controlled by polymerization techniques. Based on the above assumptions, a series of PSCC copolymers were synthesized with various contents of cationic comonomers. The effect of charge density on PSCC colloid properties was examined. The PSCC sizing performance was evaluated, and the effects of copolymer addition, charge density, particle size, drying temperature, as well as pH were discussed.

EXPERIMENTAL

Material

Styrene (Aldrich) was used as the monomer for copolymerization. It was purified by passing it through an activated neutral aluminum oxide (Aldrich) column before use. The cationic comonomer vinylbenzyl trimethylammonium chloride (VBTMAC, m/p 60/40, Acros Organics) and initiator 2, 2'-azobis (N, N'-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako Pure Chemicals) were applied as received. Ethanol was used as solvent with analytical grade. Bleached kraft softwood (BKS) pulp was used for handsheet making.

Polymer Synthesis

Copolymers of styrene and VBTMAC were synthesized by direct copolymerization of the two materials in ethanol. The details for the copolymer preparation were published previously [13]. In a typical polymerization process, a four-necked glass reactor equipped with a magnetic stir was filled with 150 ml-ethanol and an appropriate amount of styrene and VBTMAC. The solution was flashed with nitrogen for 30 minutes and thermostated at 60°C. After stabilization of temperature, VA-044 dissolved in 5 ml of deionized water was injected. The reaction was carried out under nitrogen for 4 hours with constant stirring. Finally, the solvent and excess monomers were removed by distillation under reduced pressure at 35°C. The different charge densities of copolymers were obtained by varying the ratio of cationic comonomer to the total moles of monomers. The chemicals used for the copolymerization are listed in **Table 1**.

Preparation of Colloid Dispersion

A polystyrene-based cationic copolymer (PSCC) was dispersed or dissolved in water at different temperatures until a stable colloid dispersion was reached. The preparation time was determined by heating temperature.

Polymer Characterization

The particle size of PSCC in the colloid dispersion was measured with Photon Correlation Spectroscopy using a Malvern Zetasizer 3000. The measurement was conducted at a 90-degree angle using a 633-nm He-Ne laser. The apparent charge density was determined by colloid titration using a 0.0001-N potassium polyvinyl sulfate (PVSK) solution. Toluidine blue-O (1% aqueous solution) was used as a color indicator.

Handsheet Preparation and Sizing Test

Bleached softwood kraft (BSK) pulp was used in this study. The pulp was washed extensively according to TAPPI Method T 261. The washed pulp was then diluted to a consistency of 0.3%. After adding the desired amount of PSCC, the stock was stirred for 30 s and allowed to stand for another 2 min. The handsheet was made according to TAPPI Method T 205 and dried in a hot plate for 30 min. The heating temperature varied from 110°C to 140°C based on the experimental design.

The sizing effect was evaluated by either the Hercules Sizing Test (HST) or the water absorbency of paper, according to the TAPPI methods. An HST test was conducted at 80% reflectance by using a 10% formic acid ink solution.

RESULTS/DISCUSSION

The Possible Mechanism

PSCC is a random copolymer of styrene and cationic comonomer vinylbenzyl trimethyl ammonium chloride. The polymerization reaction and chemical structure is illustrated in **Figure 1**. The possible mechanism of copolymer aggregate formation and paper sizing development with the cationic polystyrene-based copolymer is schematically shown in **Figure 2**. Because the copolymers contain a water-insoluble styrene backbone and different contents of cationically charged monomers, the copolymers can be either water-soluble or insoluble depending on the charge density, molecular weight, and structure. PSCC is a typical cationically charged hydrophobic copolymer. The hydrophobic polystyrene tends to aggregate, and the hydrophilic VBTMAC tends to dissolve in water. As a result, this copolymer is expected to form stable colloids in water if the hydrophobic/hydrophilic forces are well balanced. Because these particles are cationically charged, they can be adsorbed onto negatively charged wood fibers. When the temperature increases to the glass transition temperature or melting temperature, the copolymer defuses along the fiber surface and finally forms a hydrophobic layer on fiber surfaces (paper sizing).

PSCC Colloid Properties

The overall microstructure of these polymers is very similar to the structure of polystyrene with the exception that PSCC contains randomly distributed cationic comonomer units along a molecule chain. The details of polymerization, the physical properties of the copolymers, and the micelle-like aggregation were reported previously, and only a brief discussion was given in this communication[13].

For the charge-stabilized polymeric aggregates, charge density plays a very important role in controlling the colloidal characters of PSCC. In this study, the colloid properties of four PSCCs with cationic comonomer content ranging from 5% to 20% were examined. As shown in **Table 2**, increasing the content of cationic comonomer during polymer synthesis increased the charge density and the particle size became smaller. It is believed that, as the charge density increases, the interaction between the polymer and water molecules becomes stronger, resulting in a reduced hydrophobicity and thereby a smaller particle size. When the content of cationic comonomer reached up to 15%, PSCC completely dissolved in water.

PSCC particle size is dependent not only on the polymer charge density, but also on the temperature during dispersion preparation. This dependency was investigated using the polymer containing 10% cationic comonomer, as shown in **Figure 3**. At a temperature lower than 70°C, the polymer could not form uniform dispersion. As temperature increased, the stable colloid dispersion was obtained and the particle size was reduced. However, when the temperature reached 90°C or higher, the particle size did not change further. It implies that the kinetic aspect also influences the particle sizes even though the charge density is the dominant factor.

Sizing Development with PSCCs

Because PSCC has a polystyrene backbone, it is hydrophobic. However, because it also has cationic repeat units in the backbone, it can be adsorbed onto fiber surface. These unique properties suggest that PSCC can be used as an internal sizing agent. **Figure 4** shows some typical results of PSCC sized handsheets. In these experiments, the PSCC that contained 10% cationic comonomer was used and the addition level of PSCC ranged from 0.3% to 1.0% based on dry fiber mass. It can be seen from **Figure 4** that the sizing efficiency was increased sharply when the addition level of polymer increased from 0.3%

to 0.5%. With 0.5% polymer addition, the value of HST reached more than 2000 s, showing that PSCC with 10% cationic comonomer could be an effective sizing agent.

It is thought that, when the PSCC dispersion is added to pulp, the cationically charged polymer microaggregates adsorb onto fiber surfaces. As the polymer is heated to above the glass transition temperature (T_g), it melts and spreads and finally form a thin layer on the fiber surface. Since PSCC copolymer has a multitude of positively charged sites available for electronic neutralization, the particle can be strongly attached to the fibers even though an individual electronic attraction is weak. This feature also accelerates the polymer spreading under the influence of heat. Furthermore, the presence of multiple charge sites may prevent sizing reversion. Sizing reversion is thought to be due to the overturn of the polar groups to water molecules. In the case of PSCC sizing, even if there are some charged groups overturned, the rest still work on anchoring the sizes to fiber surfaces and sizing would not be lost. This expectation was confirmed by the fact that there was no reduction observed on the HST value when the test was repeated 10 days later.

Effect of Charge Density

As discussed earlier, the charge density determines the colloid properties of the polymer, and it must also affect the sizing performance. The water absorbency was examined on handsheets sized with four PSCC copolymers, in which the content of cationic comonomer varied from 5% to 20%. The polymer addition level was set at 0.5% for all samples. Sized handsheets were dried at 140°C for 30 minutes. As shown in **Figure 5**, either low charge density or high charge density reduced the sizing effect. Possibly, when the charge density is too low, the retention of the polymer by fibers may not be strong enough and the sizing material may be lost during handsheet making. The low charge density also leads to large colloidal aggregates that have difficulty spreading and distributing uniformly in the sized sheet during the curing process. Consequently, the sizing effect is reduced. On the other

hand, if the charge density is too high, the hydrophilicity of the polymer increases, a condition which cannot effectively prevent the penetration of water in the handsheets. Therefore, an optimum range of charge density exists for an effective sizing. As shown in **Figure 5**, both PSCC copolymers with 5% and 15% cationic comonomer have lower sizing effects than that of the copolymer with 10% comonomer. When the content of cationic comonomer reached up to 20%, no sizing effect was observed.

Effect of Particle Size

PSCC containing 10% charge density was used to test the effect of particle size on sizing. In order to obtain different particle sizes, the same polymer was dispersed in water at 80°C, 90°C, and 100°C, respectively. Handsheets were sized with the addition level of 0.5% and were dried at 140°C for 30 minutes. **Figure 6** indicates the correlation between the sizing performance and the particle size of polymer aggregates. The sizing efficiency was increased as particle size was reduced. According to the sizing mechanism, there are two possible reasons, i.e., adsorption and spreading, involved in this phenomenon. Obviously, the smaller the particle size, the easier the polymer spreads onto fiber surfaces during curing. On the other hand, the adsorption of the PCSS polymer may also be affected by the particle size. However, this factor was not examined in the present study.

Effect of Curing Temperature

Figure 7 demonstrates the effect of drying temperature on sizing. It can be seen that the sizing is more developed as drying temperature increases. The effect of drying condition can be explained by the mobility of the polymer at different temperatures. One of the characteristics of the polymer is the glass transition temperature (T_g), at which polymer molecules are capable of moving. Because the glass transition temperature of polystyrene is about 105°C, the sizing cannot be developed until the polymer spreading occurs at high temperature. This is confirmed by the fact that there was no sizing development observed

for the sheets dried at room temperature. It was also observed in this study that the higher the drying temperature, the lower the viscosity of the polymer, and the better the spreading.

Effect of pH on PSCC Sizing

The effect of pH on PSCC sizing was observed in the present study. For the sizing test, handsheets were prepared and sized under different pH conditions. The PSCCs that had 10% cationic comonomer were used. The polymer was prepared into two dispersions (controlled by the temperature used to prepare the polymer suspension) that had particle sizes of 47 nm and 30 nm, respectively. The addition level of the polymer was fixed at 0.5%. Sized handsheets were cured at 140°C for 30 minutes. As shown in **Figure 8**, for both polymer dispersions, HST values were lower at lower pH conditions. Indeed, this phenomenon was not expected to happen with a PSCC copolymer. Since the quaternary ammonium has already been electronically saturated, changing pH condition should not affect its ionization or the degree of dissolution. Thus, the charge density and hydrophobicity of the polymer should not be affected either. The explanation of pH effect may be attributed to the changes of fiber surface chemistry. It is known that the surface charge on paper fibers is due to the ionization of surface functional groups, such as a carboxyl group (COOH). The pH has a profound effect on the state of these groups. Scott [2] pointed out that most of the carboxyl groups take on a proton, and the charge becomes essentially zero at pH below 2.75. Conversely, at pH higher than 7, many of the carboxyl groups are ionized and the fiber becomes more negatively charged. These changes of the surface charge with pH would affect the adsorption of polymer molecules on fibers. High pH condition leads to a more negatively charged surface and a better retention, and therefore a higher sizing effect. At lower pH value, the lower charged fiber could not attach to as many polymers as it can at high pH; as a result, the sizing performance is reduced.

Improvement of Paper Properties by PSCC

It is of interest to examine the possible effect of PSCCs on paper properties. For evaluation, three polymers with 0.5% addition level were tested. The content of cationic comonomer of the three polymers ranged from 5% to 15%. Curing was set at 140°C for 30 minutes. For comparison, control sheets were made without polymer addition.

The addition of PSCCs also improved the tensile strength of handsheets, as shown in **Figure 9**. It is probably due to the better fiber-fiber contact by the presence of the polymer. The adhesion of polymers to fiber surfaces and the properties of the polymer itself may also have an influence on paper properties. The improvement on paper properties implies that a PSCC copolymer would work as both a sizing agent and a potential strength additive.

CONCLUSION

In this study, a series of cationic polystyrene copolymers was synthesized by varying the content of cationic comonomer. The copolymers could form stable colloids in water if the charge balance was well controlled. Charge density increased with the increase of cationic comonomer during polymerization. Charge density was the dominant factor related to PSCC colloid properties. Increased charge density of PSCC led to reduced hydrophobicity, improved solubility, and smaller particle size. Particle size was not only affected by charge density but also could be controlled by the temperature of dispersion preparation.

Sizing with PSCC copolymer was significant. There existed an optimum range of charge density for effective sizing. For the same polymer, smaller particles contributed to a higher sizing level in terms of uniform distribution and better spreading. Heat treatment was

essential for PSCC sizing. The role of heating was to increase the spreading of size over fiber surfaces. The higher the drying temperature, the higher the sizing degree. PSCC exhibited high sizing performance at high pH conditions, while moderate sizing could still be achieved at low pH.

The potential advantages of sizing with PSCC copolymers include:

- PSCC acts as a sizing agent without a need for a retention aid.
- PSCC dispersion has a long shelf life.
- A sizing effect strongly depends on the charge density and particle size of the copolymer aggregates.
- No size reversion occurs.
- Paper properties are improved with PSCC.

Although polystyrene-based cationic copolymers (PSCCs) as internal sizing agents require additional research before their commercial viability can be assessed, they appear to have considerable potential for competing against conventional sizes.

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Figure Captions

Figure 1. Polymer synthesis and chemical structure of PSCC.

Figure 2. The mechanism of cationic aggregate formation and the application as paper sizing agent.

Figure 3. Dependency of Particle Size on Temperature.

Figure 4. Sizing Development with PSCC. PSCC: 10% cationic comonomer; curing: 140°C for 30 minutes.

Figure 5. Effect of charge density on sizing. Addition level of polymer: 0.5%; curing: 140°C for 30 minutes.

Figure 6. Effect of particle size on sizing. PSCC: 10% cationic comonomer; Addition level: 0.5%; curing: 140°C for 30 minutes.

Figure 7. Effect of curing temperature on sizing. PSCC: 10% cationic comonomer; addition level: 0.5%; curing time: 30 minutes.

Figure 8. Effect of pH on sizing. 1: PSCC with 47-nm particles; 2: PSCC with 30-nm particles; addition level: 0.5%; curing: 140°C for 30 min.

Figure 9. Effect of PSCC on paper tensile strength. Sizing condition: 0.5% polymer content; curing at 140°C for 30 min.

Table 1. Chemical Usage of Copolymerization

POLYMER	A	B	C	D	E
Styrene (mmol)	108	108	108	108	108
VBTMAC (mmol)	6	12	19	27	46
VA-044 (mmol)	0.7	0.7	0.7	0.7	0.7
Ethanol (ml)	150	150	150	150	150
Ratio of VBTMAC (% total moles)	5	10	15	20	30

Table 2. Colloid Properties of PSCC

Polymer	Content of Cationic Comonomer	Charge Density (meq/g)	Particle Size* (nm)
A	5%	1.03	41
B	10%	1.21	30
C	15%	1.43	dissolved
D	20%	1.68	dissolved

* The four polymers were dispersed in water at 90°C.

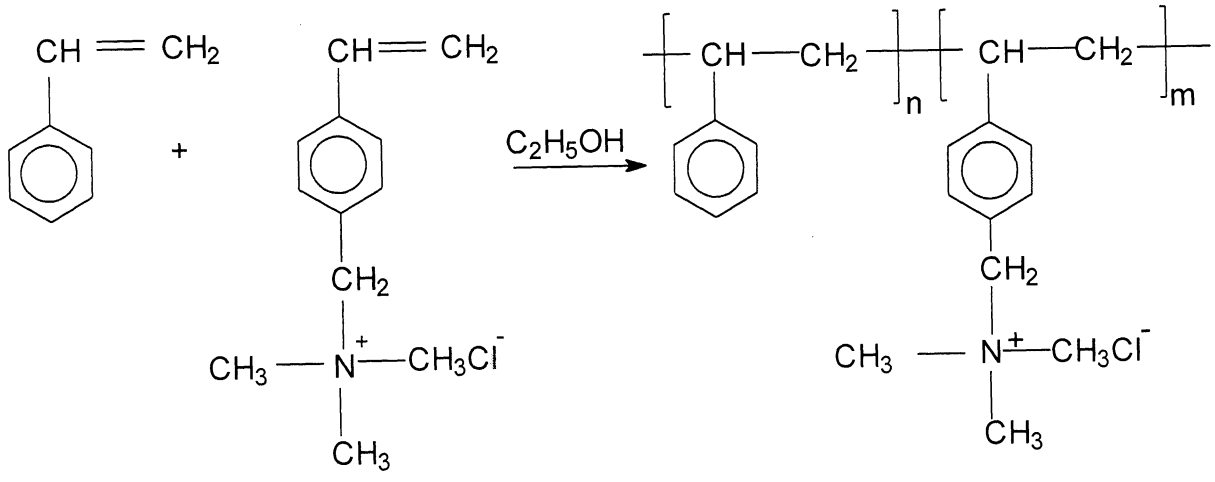

Figure 1. Polymer Synthesis and Chemical Structure of PSCC.

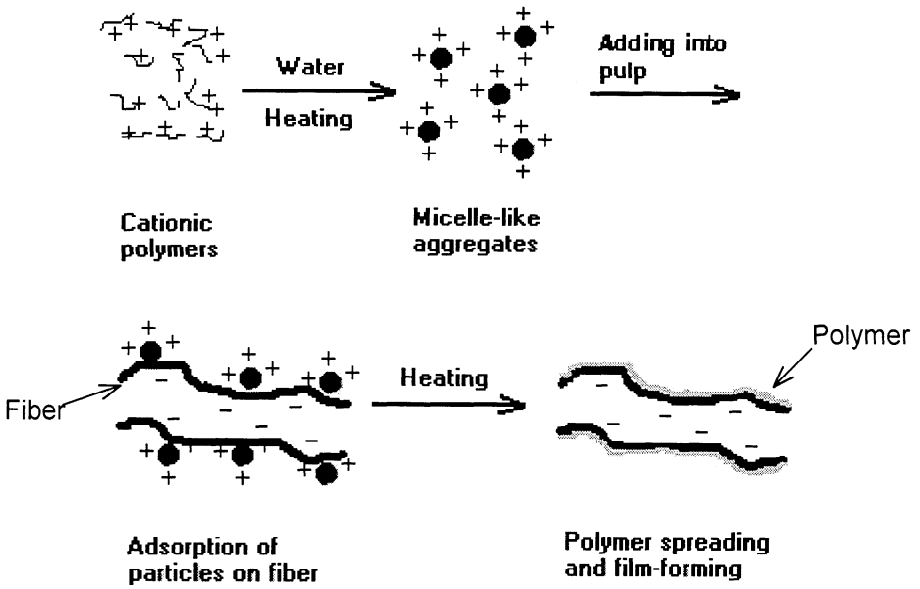

Figure 2. The mechanism of cationic aggregate formation and the application as paper sizing agent.

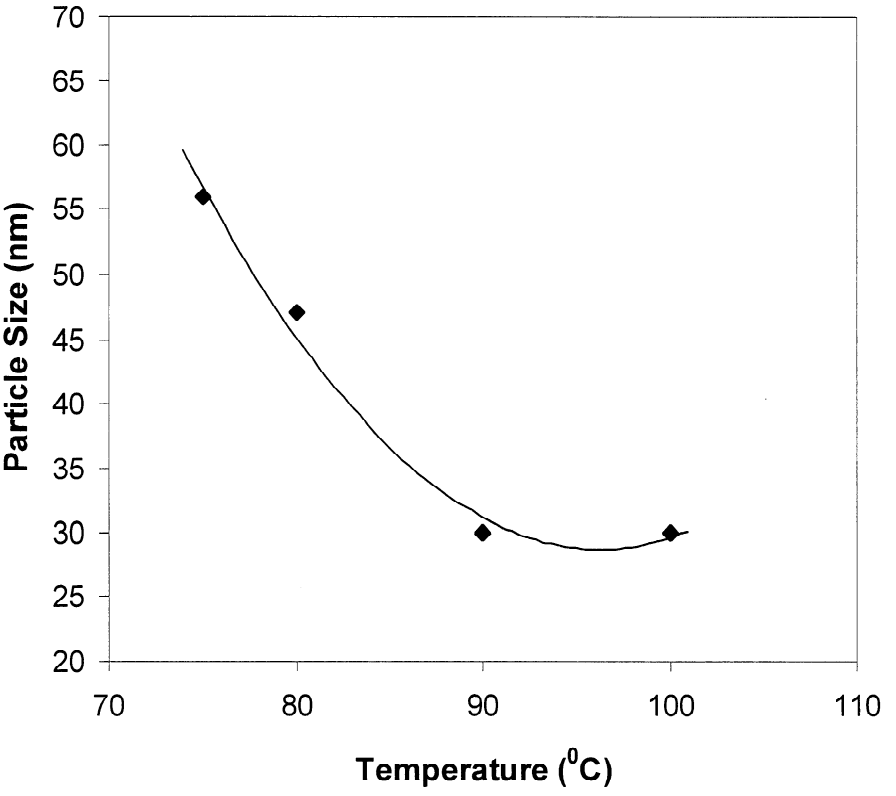

Figure 3. Dependency of Particle Size on Temperature.

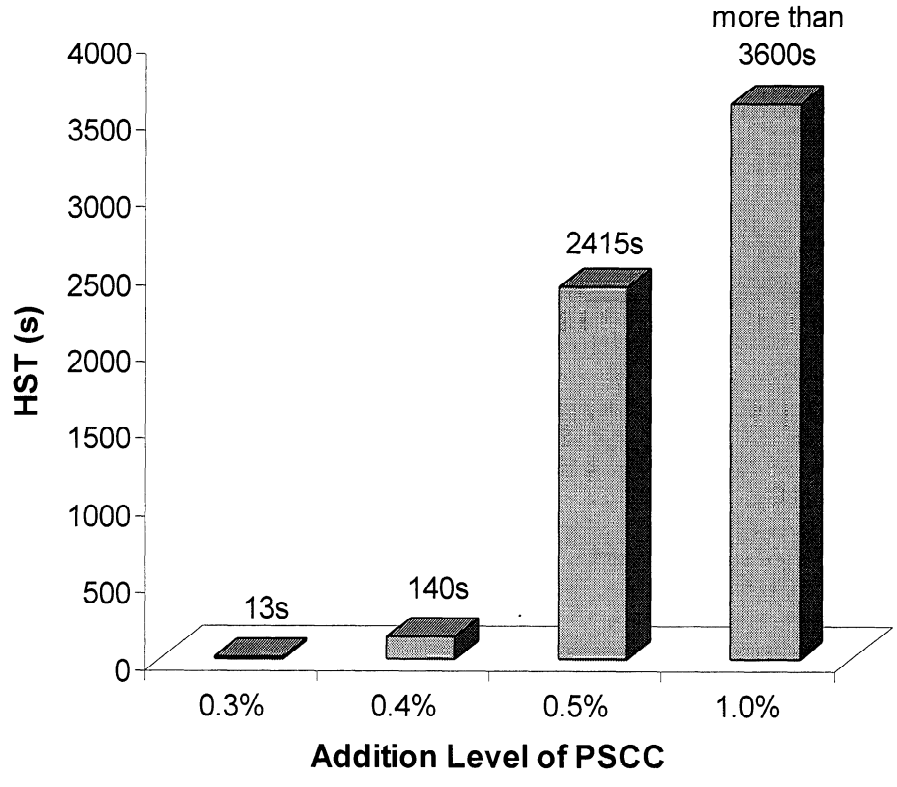

Figure 4. Sizing Development with PSCC. PSCC: 10% cationic comonomer; curing: 140°C for 30 minutes.

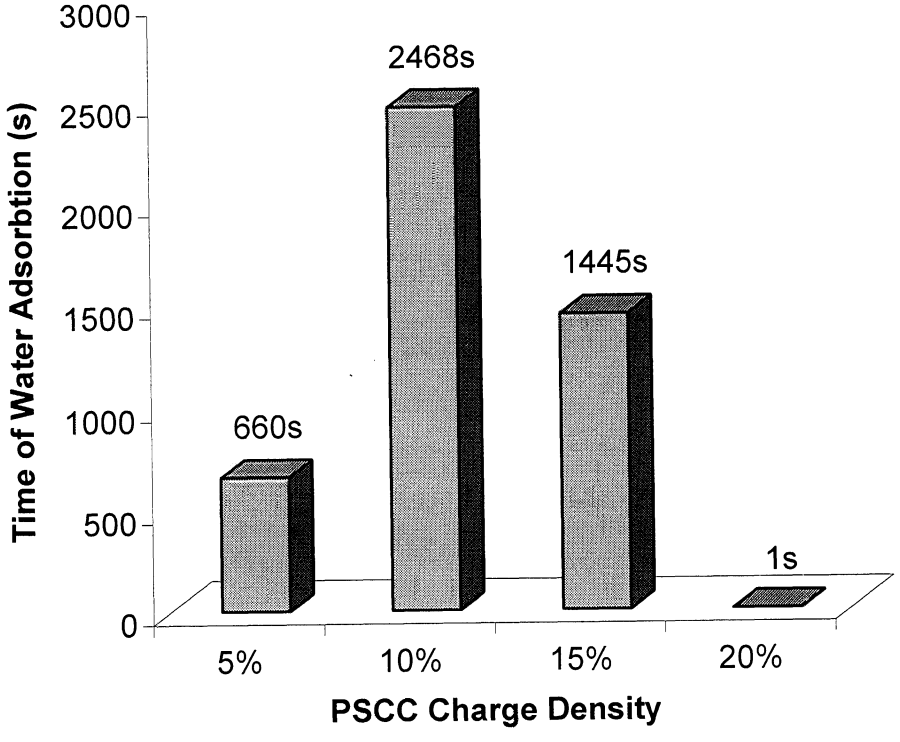

Figure 5. Effect of Charge Density on Sizing. Addition level of polymer: 0.5%; curing: 140°C for 30 minutes.

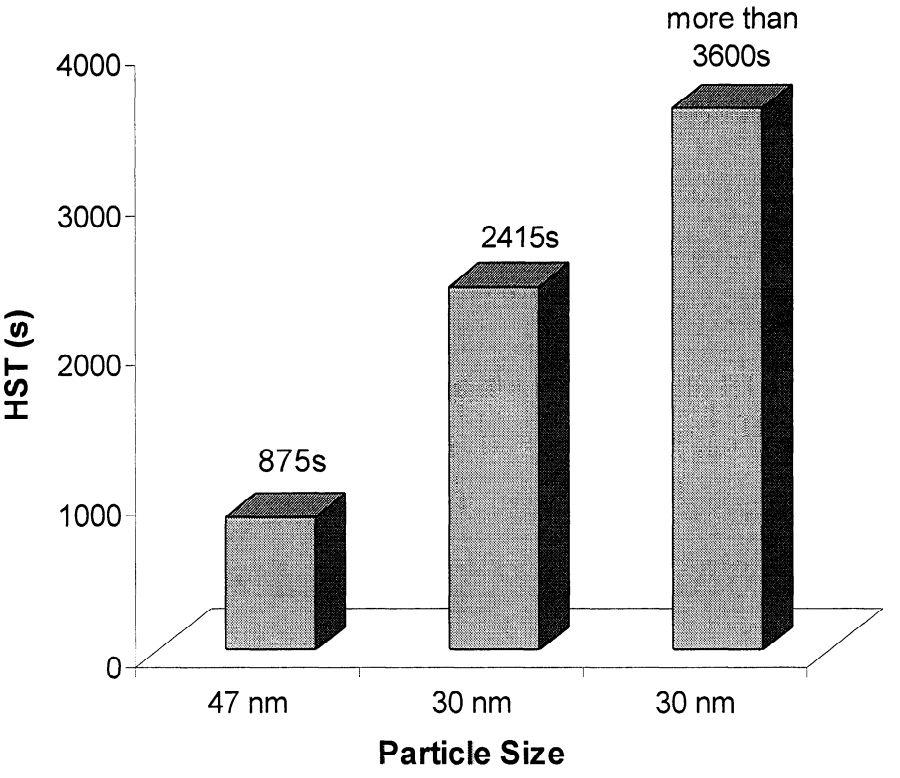

Figure 6. Effect of Particle Size on Sizing. PSCC: 10% cationic comonomer; Addition level: 0.5%; Curing: 140°C for 30 minutes.

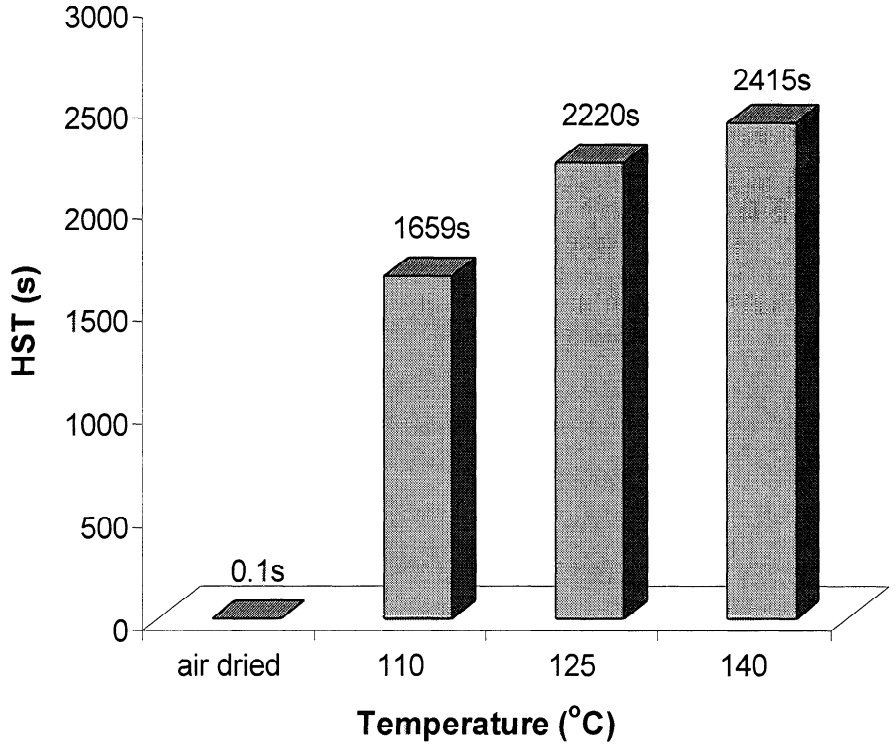

Figure 7. Effect of Curing Temperature on Sizing. PSCC: 10% cationic comonomer; addition level: 0.5%; curing time:30 minutes.

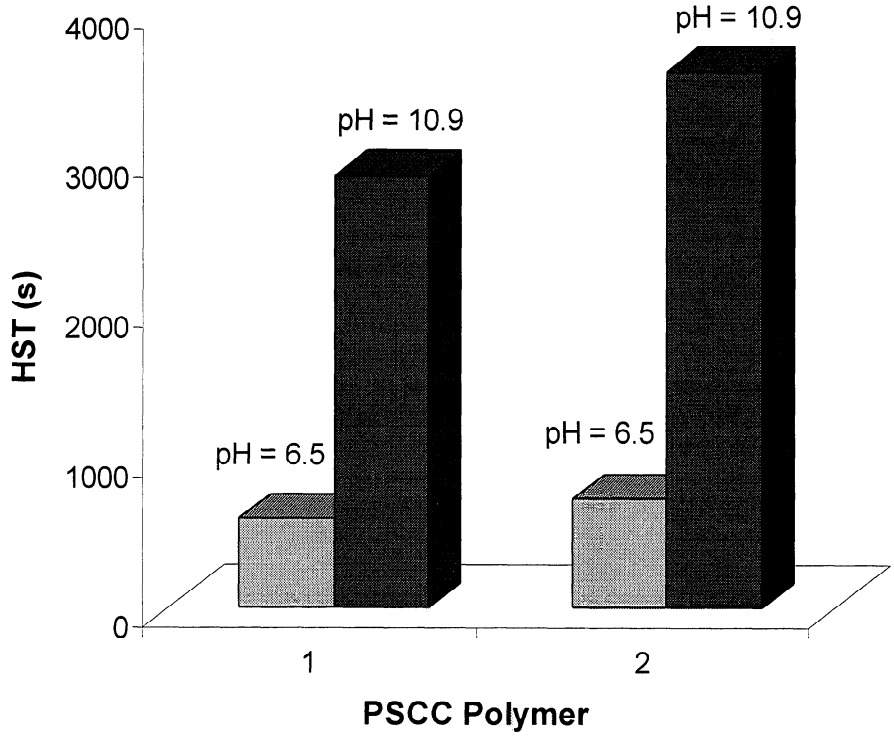

Figure 8. Effect of pH on Sizing. 1: PSCC with 47 nm particles; 2: PSCC with 30 nm particles; addition level: 0.5%; curing: 140°C for 30 min.

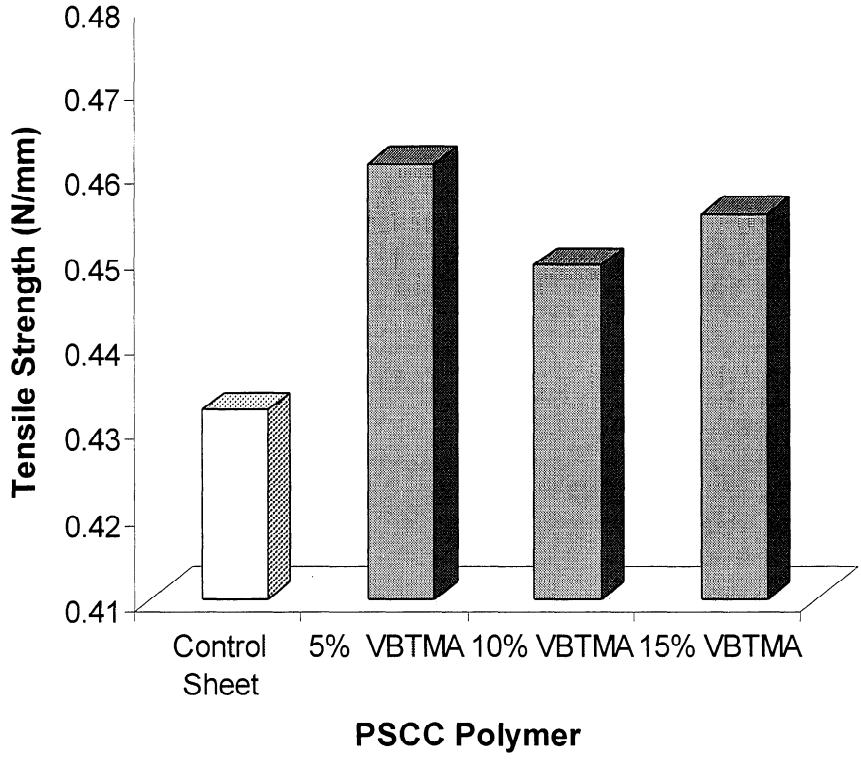

Figure 9. Effect of PSCC on Paper Tensile Strength. Sizing condition: 0.5% polymer content; curing at 140°C for 30 min.